Registry No. 2-Iodooctane, 557-36-8; 2-bromooctane, 557-35-7; octane, 111-65-9; 1-octene, 111-66-0; *cis*-2-octene, 7642-04-8; *trans*-2-octene, 13389-42-9; (*d,l*)-7,8-dimethyltetradecane, 82294-06-2; di-*sec*-octylmercury, 82294-07-3; tetramethylammonium perchlorate, 2537-36-2; tetrabutylammonium perchlorate, 1923-70-2; diethyl malonate, 105-53-3; 2-octanol, 123-96-6; 1,1,1,3,3-pentadeuterio-2-iodooctane, 82294-08-4; iodine, 7553-56-2; *sec*-octyl carbanion, 82294-09-5; *meso*-7,8-dimethyltetradecane, 82294-10-8.

m-Chloroperoxybenzoic Acid Oxidation of *S*-Phenyl 2,2-Dimethylpropanethiosulfinate[1,2]

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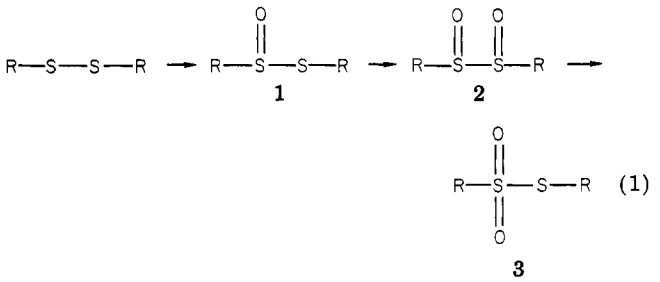
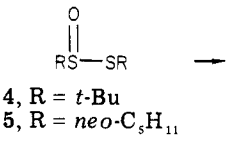
At −30 °C under nitrogen in $CDCl_3$ the *m*-chloroperoxybenzoic acid (MCPBA) oxidation of *S*-phenyl 2,2-dimethylpropanethiosulfinate (**18**) leads to *S*-(2,2-dimethylpropyl) 2,2-dimethylpropanethiosulfonate (**9**), **18**, *S*-phenyl 2,2-dimethylpropanethiosulfonate (**19**), 2,2-dimethylpropanesulfinic acid (**20**), and 2,2-dimethylpropanesulfonic acid (**21**). These products are consistent with attack by MCPBA at the sulfenyl sulfur atom of **18** to give α-disulfoxides **28** and at the sulfinyl sulfur atom of **18** to give **19**. At 24 °C, **18** reacts with **20** to give **19** and 2,2-dimethylpropanesulfenic acid (**33**), which dimerizes to *S*-(2,2-dimethylpropyl) 2,2-dimethylpropanethiosulfinate (**5**). Possible concerted, ionic, and radical mechanisms for these observations are discussed.

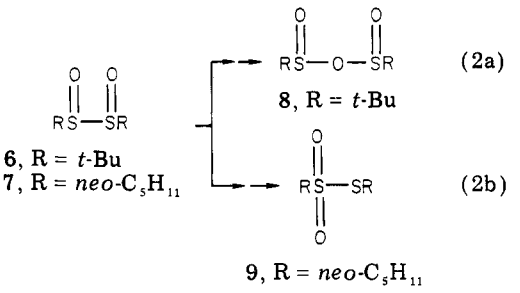
The role of α-disulfoxides (**2**) in the peroxy acid oxidation of disulfides or thiosulfinates (**1**) to thiosulfonates (**3**)[3–24] (eq 1) and in other systems[25–28] is a topic of considerable interest. Diastereomeric α-disulfoxides (**6**, **7**) have been detected via low-temperature ^1H NMR and ^{13}C NMR studies of the *m*-chloroperoxybenzoic acid (MCPBA) oxidation of *S*-(2-methyl-2-propyl) 2-methyl-2-propanethiosulfinate (**4**)[3] and *S*-(2,2-dimethylpropyl) 2,2-dimethylpropanethiosulfinate (**5**), respectively[5,7] (eq 2).



1 2 3 (1)



4, R = *t*-Bu
5, R = *neo*-C_5H_{11}



8, R = *t*-Bu (2a)

6, R = *t*-Bu
7, R = *neo*-C_5H_{11}

9, R = *neo*-C_5H_{11} (2b)

In symmetrical alkanethiosulfinates (**1**, **4**, **5**), an electrophilic oxidation would be expected to take place preferentially at the electron-rich sulfenyl sulfur atom, while a nucleophilic oxygenation could occur at the electron-poor sulfinyl sulfur atom.[3,5,16–19] However, one cannot unequivocally expect that electrophilic oxidation of an aryl

(1) Abstracted from the Ph.D. Thesis of C.N.A. University of California, Irvine, CA, 1982.
(2) Presented in part at the Second Chemical Congress of the North American Continent, Las Vegas, NV, Aug. 28, 1980, and the 8th Annual Meeting of NOBCChE, Chicago, IL, Apr 24, 1981.
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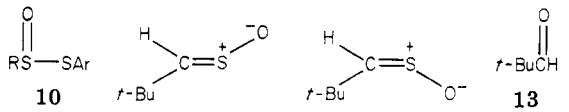
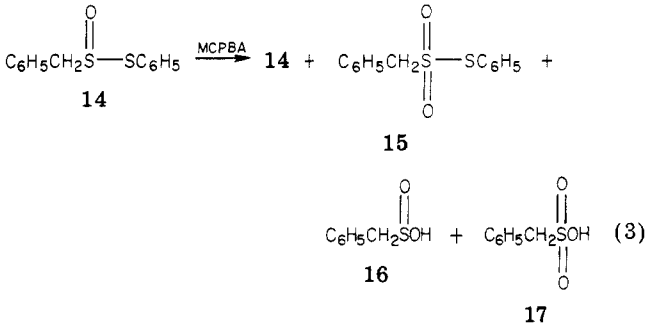
alkanethiosulfinate (10) by MCPBA would occur at sul-



10 11 12 13

fenyl sulfur rather than at sulfinyl sulfur.[4,24] It may be possible that the sulfenyl sulfur atom in 10, owing to conjugation with the phenyl ring, may actually be less electron rich than the sulfinyl sulfur atom which is attached to the electron-releasing alkyl group.

Although (*E*)- and (*Z*)-2,2-dimethylpropanethial *S*-oxides (11 and 12), 2,2-dimethylpropanal (13), and other products have been observed in the low-temperature MCPBA oxidation of 5,[5,7] the corresponding sulfines have not been detected in significant amounts in the MCPBA oxidation of *S*-phenyl phenylmethanethiosulfinate (14, eq 3).[4,24]



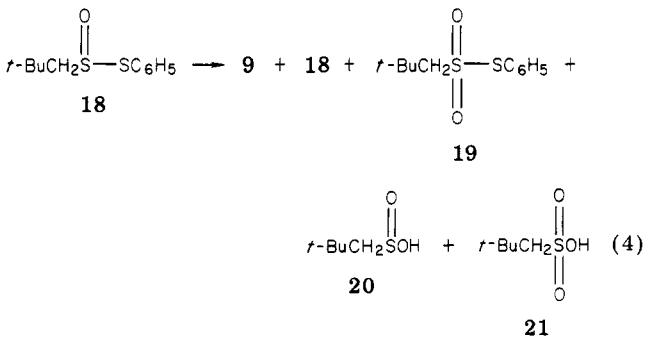
14 15 16 17 (3)

In order to determine the regiospecifity of MCPBA oxidation, the intermediacy or absence of α-disulfoxides 2, and the presence or absence of sulfines 11 and 12, we have investigated the low-temperature MCPBA oxidation of *S*-phenyl 2,2-dimethylpropanethiosulfinate (phenyl neopentanethiosulfinate, 18).

Results

The 1 equiv MCPBA oxidation of 18 was performed at −30 °C in $CDCl_3$ under a nitrogen atmosphere for 1 h. The product mixture was filtered in an inert atmosphere at −45 °C as quickly as possible in order to remove *m*-chlorobenzoic acid (MCBA). The ^1H NMR and ^{13}C NMR spectra of the filtrate were recorded as soon as possible after filtration.

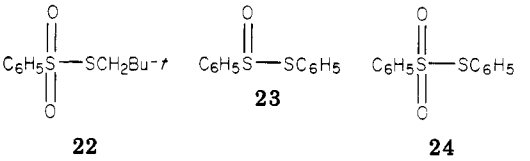
NMR analyses showed that the product mixture (Table I) contained *S*-(2,2-dimethylpropyl) 2,2-dimethylpropanethiosulfonate (9), 18, *S*-phenyl 2,2-dimethylpropanethiosulfonate (19), 2,2-dimethylpropanesulfinic



18 9 19 20 21 (4)

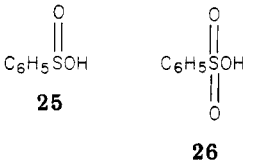
acid (20), and 2,2-dimethylpropanesulfonic acid (21). It is seen from the ^1H NMR data in Table I that as the temperature was raised, the concentration of 18 decreased, the concentration of 19 increased, and the concentrations of 9, 20, and 21 remained essentially the same.

In another experiment, 18 was oxidized with 1 equiv of MCPBA under nitrogen at −30 °C in $CDCl_3$. After 1 h most of the MCPBA had been consumed (iodometric assay). The product mixture, which was not filtered to remove MCBA, was warmed to 0 °C and stirred with 5% $NaHCO_3$ solution for 10 min, and the layers were separated. The organic phase was analyzed via HPLC, ^1H NMR, ^{13}C NMR, and IR. These analyses (Table II) showed the presence of MCBA, 9, 11–13, 18, 19, *S*-(2,2-dimethylpropyl) benzenethiosulfonate (22), *S*-phenyl



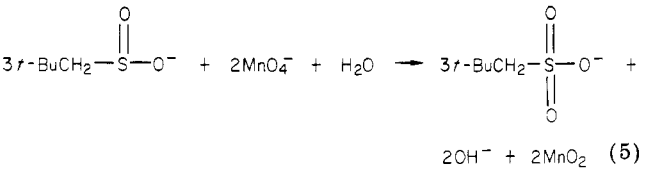
22 23 24

benzenethiosulfinate (23), and *S*-phenyl benzenethiosulfonate (24) in the organic layer. Analysis of the aqueous layer via ^1H NMR showed that the sodium salts of MCBA, 20, and 21 were present and that the salts of benzenesulfinic acid (25) and benzenesulfonic acid (26) were ab-



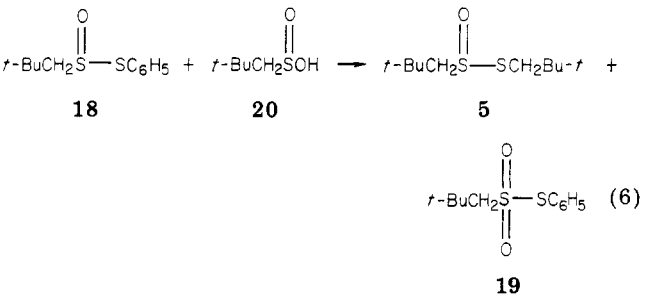
25 26

sent. The yield of 20 was also determined by permanganate ion titration (eq 5).[29]



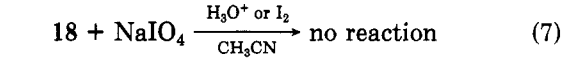
(5)

Equimolar amounts of 18 and 20 were mixed at 24 °C in $CDCl_3$, and the reaction was monitored by ^1H NMR. The products were 5 and 19 (eq 6).



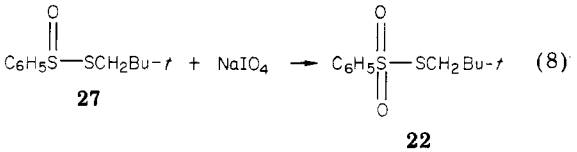
18 20 5 19 (6)

Attempted conversion of 18 to 19 with $NaIO_4$ for 2 days at 25 °C was unsuccessful (eq 7).[30,31] In contrast, *S*-



(7)

(2,2-dimethylpropyl) benzenethiosulfinate (27) was oxidized to 22 in quantitative yield.



27 22 (8)

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Table I. ^{1}H NMR and ^{13}C NMR Chemical Shifts of the Products from the MCPBA Oxidation of 18 in $CDCl_3$ [a]

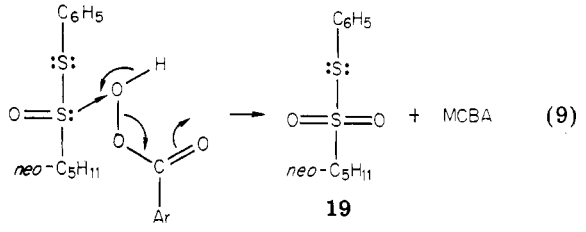
compd	no.	chemical shift,[d] δ: ^{1}H NMR (−30 °C, 105 min[b,c])	^{13}C NMR (−30 °C, 110 min[b])	^{1}H NMR (25 °C, 3 h[b,e])	^{13}C NMR (25 °C, 3 h 35 min)
t-$BuCH_2S(O)_2SCH_2Bu$-*t*	9	3.11, 3.38 (7)		3.10, 3.35 (5)	
t-$BuCH_2S(O)SC_6H_5$	18	3.18,[f] 3.24 (32)	69.85 (30)	3.13,[g] 3.22 (29)	70.67 (21)
t-$BuCH_2S(O)_2SC_6H_5$	19	3.29 (28)	71.53 (47)	3.27 (36)	72.45 (56)
t-$BuCH_2S(O)OH$	20	2.92 (18)	71.38 (17)	2.90 (17)	72.30 (15)
t-$BuCH_2S(O)_2OH$	21	3.07 (12)	63.73 (6)	3.06 (13)	64.26 (8)

[a] Me_4Si used as an internal standard; spectrometer frequency 250 (^{1}H) and 62.89 MHz (^{13}C); 200 scans were taken in 15 min for ^{13}C spectra. Only the methylene carbons and hydrogens are tabulated. Overlapping peaks preclude analysis of the aryl compounds which were analyzed via HPLC in another experiment. [b] Time after filtering the product mixture at −45 °C. [c] The product mixture was stored at −55 °C for 103 min before the ^{1}H NMR spectrum was taken. [d] Percent relative integral in parentheses. [e] The temperature was raised to 25 °C at 2 h and 10 min after filtering at −45 °C. [f] J = 13.4 Hz. [g] J = 13.6 Hz.

Discussion

In contrast to the MCPBA oxidation of symmetrical dialkyl thiosulfinates (**2**),[3,5,7] the oxidation of **14**[4,24] and **18** does not proceed at an appreciable rate at −40 °C. However, at −30 °C, MCPBA oxidized **18** to thiosulfonate **19**, sulfinic acid **20**, and sulfonic acid **21**. Table I shows that thiosulfonate **9** and reactant **18** are also components of the product mixture. This product distribution is similar to that observed in the MCPBA oxidation of **14**.[4,24]

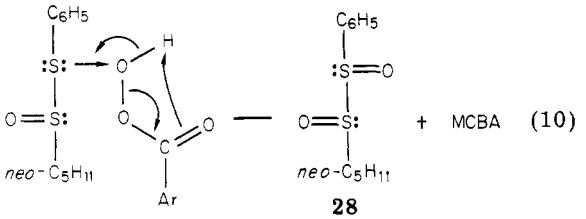
The presence of **20** and **21** in the product mixture suggests that **18** is not oxidized by MCPBA *exclusively* at the sulfinyl group (eq 9) to give **19** but that oxidation also



(9)

18 **19**

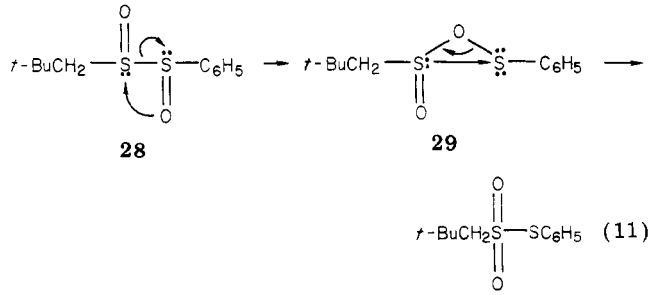
occurs at sulfenyl sulfur to yield metastable diastereomeric 2,2-dimethylpropyl phenyl disulfoxide **28** (eq 10).[3-7,16-19,24,32]



(10)

18 **28**

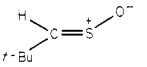
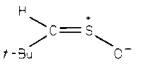
Although two isomeric sulfenyl sulfinates are possible, it appears that α-disulfoxide **28** rapidly isomerizes preferentially to *S*-phenyl 2,2-dimethylpropaneperoxythiosulfinate **29** (eq 11).[4,16,33] Homolytic dissociation of α-



28 **29** **19** (11)

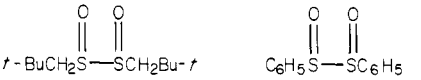
(32) Diastereomeric α-disulfoxides may be produced.

Table II. Products from the MCPBA Oxidation of 18 in $CDCl_3$ Followed by Treatment with $NaHCO_3$ Solution[a]

compd	no.	yield, %[b]: ^{1}H NMR[c]	HPLC[d]
t-$BuCH_2S(O)_2SCH_2Bu$-*t*	9	6	
	11	1	
	12	2	
t-BuC(O)H	13	3	
t-$BuCH_2S(O)SC_6H_5$	18	22	21
t-$BuCH_2S(O)_2SC_6H_5$	19	43	65
t-$BuCH_2S(O)OH$	20	14 (14)[e]	
t-$BuCH_2S(O)_2OH$	21	8	
$C_6H_5S(O)_2SCH_2Bu$-*t*	22	2	
$C_6H_5S(O)SC_6H_5$	23		3
$C_6H_5S(O)_2SC_6H_5$	24		12

[a] Reaction temperature −30°C; spectrometer frequency 250 MHz. [b] Based on moles of starting material **18**. [c] ^{1}H NMR yields (±3%) are given. Approximately 10% MCBA remained in the organic phase. [d] Analysis was done within 5 min after separation of the layers. [e] Yield based on MnO_4^- titration.

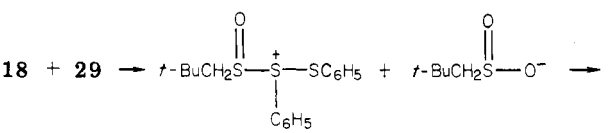
disulfoxide **28**, followed by very rapid radical recombination in a solvent cage to give 2,2-dimethylpropyl disulfoxide (**30**) and diphenyl disulfoxide (**31**), can compete with the process shown in eq 11.[23,24,34]



30 **31**

$$\mathbf{28} \xrightarrow{\text{fast}} [t\text{-}BuCH_2S\dot{O}\ \dot{O}SC_6H_5] \xrightarrow[\text{solvent cage}]{} \text{sulfenyl sulfinates and/or } \mathbf{9} + \mathbf{19} + \mathbf{22} + \mathbf{24} \quad (12)$$

Sulfenyl sulfinate **29** can isomerize to thiosulfonate **19** via a concerted mechanism (eq 11) or by reaction with **18**, possibly via an ionic mechanism (eq 13).[4]

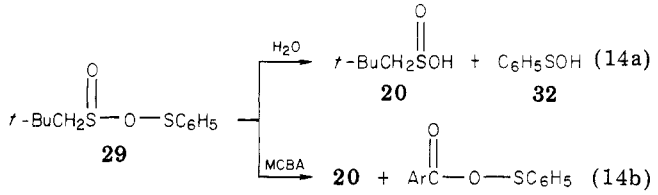


18 + **19** (13)

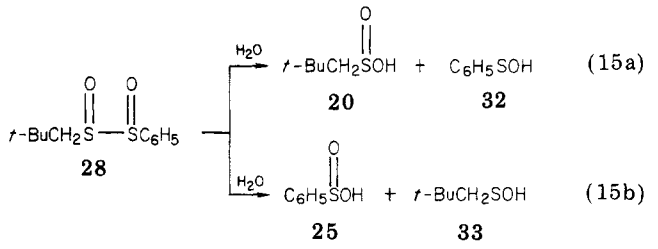
(33) The preferential formation of sulfenyl sulfinate **29** may be the result of the electron-releasing effect of the neopentyl group and/or a more favorable electronic interaction of the sulfenyl sulfur atom with the phenyl group.

(34) Howard, J. A.; Furimsky, E. *Can. J. Chem.* **1974**, *52*, 555.

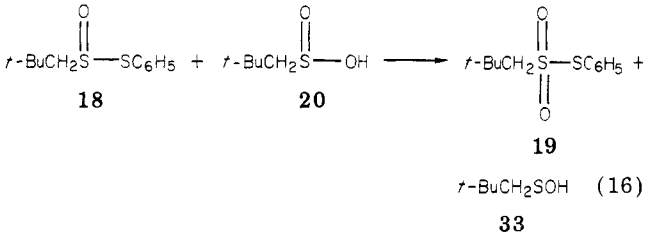
Sulfinic acid **20** could easily result from the reaction of **29** with either MCBA or trace amounts of water (eq 14).[4]



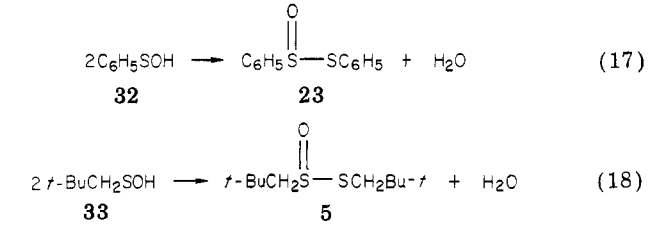
Benzenesulfenic acid (**32**) may be formed from the hydrolysis of **28** (eq 15) or **29** (eq 14). Hydrolysis of **28** can



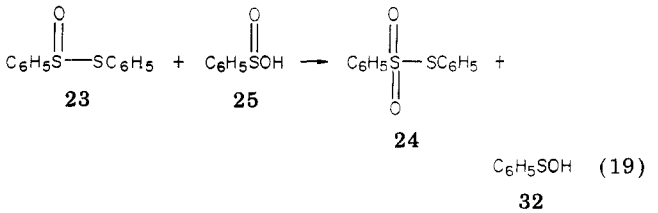
lead to **20**, **25**, **32**, and 2,2-dimethylpropanesulfenic acid (**33**). Sulfenic acid **33** may be produced by the reaction shown in eq **16** (cf. eq 6) or by hydrolysis of **30**. Hydrolysis of **30** can also lead to benzenesulfenic acid (**32**).



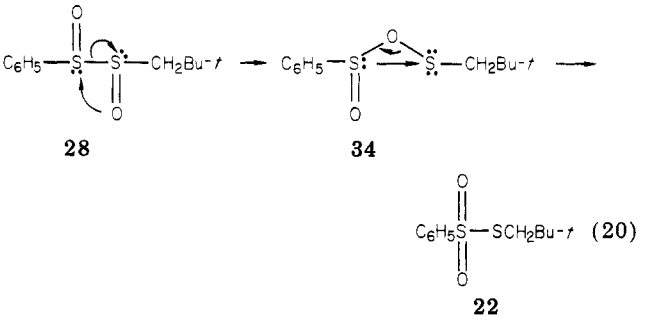
Sulfenic acid **32** or **33** can undergo dehydration to give symmetrical thiosulfinate **23** or **5** (eq 6, 16, 18), respectively.[35] The dehydration of **32** and **33** can lead to **18** and *S*-(2,2-dimethylpropyl) benzenethiosulfinate [$C_6H_5S(O)SCH_2C(CH_3)_3$].



The reaction between **18** and **20** (eq 6, 16, 18) can account for the formation of thiosulfinate **5**, which may be oxidized to thiosulfonate **9**,[7] and thiosulfonate **19**, while thiosulfonate **24** may arise from the reaction of **23** and **25** (eq 19). Thiosulfonate **22** can result from the rearrangement of α-disulfoxides **28** to *S*-(2,2-dimethylpropyl) benzenethioperoxysulfinate **34** (eq 20; cf. eq 11).[4,16,33] The sulfinyl radicals formed in eq 12 may undergo noncage intermolecular recombination to form sulfenyl sulfinates

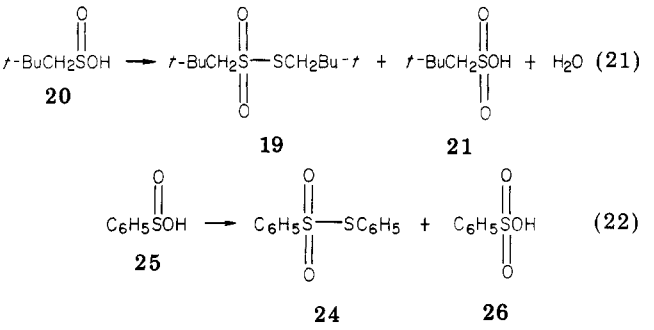


(35) Davis, F. A.; Jenkin, R. H., Jr. *J. Am. Chem. Soc.* **1980**, *102*, 7967.
(36) This reaction is being investigated.



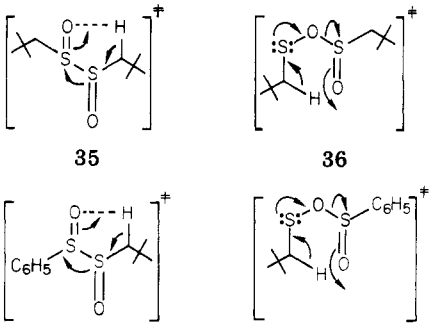
29 and **34** which then rearrange to thiosulfonates **19** (eq 11) and **22** (eq 20), respectively. The combination of two 2,2-dimethylpropanesulfinyl radicals (eq 12) would lead to α-disulfoxides **30** which can rearrange to thiosulfonate **9**.

Oxidation of sulfinic acid **20** could lead to sulfonic acid **21**. Moreover, sulfinic acids are thermally unstable and are known to disproportionate to thiosulfonates and sulfonic acids (eq 21, 22).[37-39] Disproportionation is expected

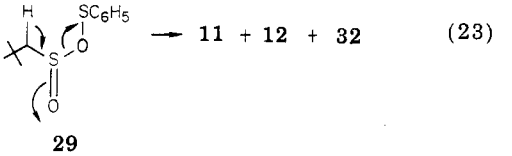


to be rapid in the presence of a strong acid in an aprotic solvent.

Although activated complexes **35** and **36** have been



proposed to explain the formation of sulfines **11** and **12** during the MCPBA oxidation of **5**,[3,5,7] sulfenyl sulfinate **29** does not possess the requisite hydrogen atom for cycloelimination. However, **29** may simply eliminate **32** and form **11** and **12** (eq 23). α-Disulfoxide **28** (cf. **37**), α-di-



sulfoxide **30** (cf. **35**), and sulfenyl sulfinate **34** (cf. **38**) are capable of undergoing cycloelimination to give the small

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amounts of sulfines 11 and 12 which are formed during the oxidation of 18 (Table II).[3,4,7,40-43]

Experimental Section

Melting points were obtained on a Thomas-Hoover melting point apparatus and are uncorrected. Elemental analyses were performed by Robertson Laboratory, Florham Park, NJ.

Mass spectra were obtained on a Finnigan GC/EI-CI mass spectrometer with a Nova 3 data system.[44] NMR spectra were obtained on Bruker WH-90 and WM-250 Fourier transform NMR spectrometers which were controlled by B-NC-12 and Bruker Aspect 2000 computers, respectively, and on a Varian EM-360 NMR spectrometer.[45,46] IR spectra were obtained on a Perkin-Elmer 283 spectrometer.

HPLC was accomplished on an EM Hibar silica gel analytical column with 3% ethyl acetate–isooctane as the eluant. Flash column chromatography was modified as follows: the material to be separated was placed on top of the column (400-mesh EM silica gel) without preadsorption. The elution rate was 0.5 in. of column length per minute regardless of the diameter of the column. Analytical TLC was performed on Analtech silica gel coated (25 μm) prescored slides. Preparative TLC was done on commercial 250-μm silica gel plates.

Commercial (Aldrich) $CDCl_3$ was used. Other reagents and solvents were purified by standard procedures.

***S*-(2,2-Dimethylpropyl) 2,2-Dimethylpropanethiosulfinate (5).** Oxidation of neopentyl disulfide (**39**)[47] with 1 equiv of MCPBA in $CHCl_3$ at 0 °C gave **5**, which was purified by flash chromatography on silica gel. Recrystallization from hexane gave **5**: 66%; mp 68–69 °C; IR ($CDCl_3$) 1060 cm^{-1} (S=O); CI mass spectrum (*i*-C_4H_{10}), *m/z* 223 (MH^+); ^1H NMR ($CDCl_3$) δ 1.03 [s, 9 (CH_3)$_3$ on sulfenyl side of **5**], 1.14 [s, 9 (CH_3)$_3$ on sulfinyl side of **5**], 3.01, 3.16, [d, 2, *J* = 4.2 Hz, CH_2–S–S(O)], 3.06 3.11 (d, 2, *J* = 13.2 Hz, CH_2–S(O)–S); ^{13}C NMR ($CDCl_3$) on sulfenyl side of **5** δ 28.72 [C(CH_3)$_3$], 32.07 [C(CH_3)$_3$], 46.93 (CH_2), on sulfinyl side of **5** δ 29.56 [(CH_3)$_3$], 32.26 [C(CH_3)$_3$], and 70.42 (CH_2).[5,45,46]

***S*-(2,2-Dimethylpropyl) 2,2-dimethylpropanethiosulfonate (9)** was prepared as previously described.[5]

***S*-Phenyl 2,2-dimethylpropanethiosulfinate (18)** was prepared by a modification of the method of Backer and Kloosterziel.[48] A solution of thiophenol (1.54 mL, 15 mmol) and pyridine (1.22 mL, 15 mmol) in 30 mL of ether was cooled to 0 °C. Neopentanesulfinyl chloride (2.3 g, 15 mmol) dissolved in 20 mL of ether was added dropwise with stirring. The mixture was stirred for another 30 min at 0 °C and another 15 min at 24 °C. After filtration, the ether solution was washed successively with ice-cold 1 M H_2SO_4 (10 mL), ice-cold 5% $NaHCO_3$ (10 mL), and water (10 mL). Compound **18** was isolated in 87% yield as a solid after flash column chromatography and low-temperature crystallization from hexane: mp 36–38 °C; IR ($CHCl_3$) 1065 cm^{-1} (S=O); CI mass spectrum (*i*-C_4H_{10}) *m/z* 229 (MH^+); ^1H NMR ($CDCl_3$) δ 1.14 (s, 9, *t*-Bu), 3.04, 3.22 [d, 2, *J* = 13.2 Hz, CH_2–S(O)], 7.27–7.48, 7.58–7.66, (m, 5, Ar H); ^{13}C NMR ($CDCl_3$) δ 29.56 (C(CH_3)$_3$), 32.18 (C(CH_3)$_3$), 70.42 (CH_2).[45,46]

***S*-Phenyl 2,2-dimethylpropanethiosulfonate (19)** was prepared from the reaction of neopentanesulfinic acid (**20**) with thiophenol:[24] 59% yield; mp 87–88 °C.

Anal. Calcd for $C_{11}H_{16}O_2S_2$: C, 54.06; H, 6.60. Found: C, 53.28; H, 6.71.

Attempted preparation of **19** via the $NaIO_4$ oxidation of **18** in aqueous acetonitrile by using concentrated HCl or iodine as catalyst at 25 °C for 2 days was unsuccessful.[31]

2,2-Dimethylpropanesulfinic acid (20) was prepared in quantitative yield by the reaction of NaOEt with phthalimidomethylneopentyl sulfone in EtOH.[5,49]

2,2-Dimethylpropanesulfonic acid (21) was prepared by oxidation of neopentanethiol (**39**) with HNO_3.[5,50]

***S*-(2,2-Dimethylpropyl) benzenethiosulfonate (22)** was prepared from the acid (concentrated HCl) catalyzed $NaIO_4$ oxidation of *S*-(2,2-dimethylpropyl) benzenethiosulfinate (**27**) in aqueous acetonitrile.[31] Thiosulfonate **22** was obtained as a colorless oil in quantitative yield after flash chromatography. Prolonged exposure (>10 min) to silica gel led to decomposition: IR (neat) 1130, 1330 cm^{-1} (SO_2); ^1H NMR ($CDCl_3$) δ 0.92 [s, 9, (CH_3)$_3$], 2.96 (s, 2, CH_2), 7.4–8.1 (m, 5, Ar H); ^{13}C NMR ($CDCl_3$) δ 28.72 [C(CH_3)$_3$], 31.93 [C(CH_3)$_3$], 49.57 (CH_2), 126.9–145.1 (benzene carbons).[45,46]

***S*-Phenyl benzenethiosulfinate (23)** was prepared as previously described.[48,51]

***S*-Phenyl benzenethiosulfonate (24)** was prepared as previously described.[52]

Benzenesulfinic acid (25) was obtained commercially as its sodium salt. **Benzenesulfonic acid (26)** is also commercially available.

***S*-(2,2-Dimethylpropyl) benzenethiosulfinate (27)** was prepared by coupling 2,2-dimethylpropanethiol (**40**) and benzenesulfinyl chloride (**41**) in the presence of pyridine.[48] The same procedure used for the preparation of **18** was employed. Compound **27** was isolated as a light yellow oil in 50% yield after flash chromatography on silica gel: IR ($CHCl_3$) 1088 cm^{-1} (S=O); ^1H NMR ($CDCl_3$) δ 1.03 [s, 9 (CH_3)$_3$], 2.99, 3.16 (d, 2, CH_2 *J* = 13.2 Hz), 7.48–7.54, 7.73–7.77 (Ar H); ^{13}C NMR ($CDCl_3$) δ 28.75 [C(CH_3)$_3$], 32.15 [C(CH_3)$_3$], 47.09 (CH_2), 124.3–144.9 (benzene carbons).[45,46]

Bis(2,2-dimethylpropyl) disulfide (39) was prepared by oxidation of 2,2-dimethylpropanethiol (**40**) with iodine:[53,54] ^1H NMR ($CDCl_3$) δ 1.02 [s, 9, (CH_3)$_3$], 2.76 (s, 2, CH_2); ^{13}C NMR ($CDCl_3$) δ 28.83 [C(CH_3)$_3$], 30.31 [C(CH_3)$_3$], 55.96 (CH_2).[5,45,46]

2,2-Dimethylpropanethiol (40) was prepared from neopentyl tosylate as previously described.[5,55,56]

2,2-Dimethylpropanesulfinyl chloride (41) was prepared by the procedure of Douglass and Norton,[57] except CH_2Cl_2 was used as the solvent. Compound **41** was obtained in 83% yield; bp 60–61 °C (5 mm). ^{13}C NMR ($CDCl_3$) δ 29.55 [C(CH_3)$_3$], 32.73 [C(CH_3)$_3$], 79.24 (CH_2).[5]

Oxidation of *S*-Phenyl 2,2-Dimethylpropanethiosulfinate (18). Method A. Treatment with $NaHCO_3$ Solution.[5] In a nitrogen atmosphere, **18** (0.320 g, 1.40 mmol) was dissolved in 2 mL of $CDCl_3$ and cooled to −30 °C in a dry ice/2-propanol bath. A solution of 82% MCPBA (0.293 g, 1.40 mmol) dissolved in 5.0 mL of $CDCl_3$ was added slowly with stirring. The reaction mixture was stirred for 1 h at −30 °C and warmed to 0 °C, and 7 mL of an ice-cold 5% solution of $NaHCO_3$ in D_2O was added. Stirring was continued for 10 min, the layers were separated, and the organic phase was dried (Na_2SO_4). The organic layer was analyzed within 5 min after separation via ^1H NMR and HPLC. The aqueous layer was analyzed by ^1H NMR, diluted with 300 mL of 0.1 M NaOH, and titrated potentiometrically with 0.008 M $KMnO_4$, which was standardized by titration with a known amount of benzenesulfinic acid (**25**). A silver–platinum electrode was used,[58] and the first jump in potential was used as the equivalence point.

Method B. Low-Temperature NMR Experiment.[5] In a nitrogen atmosphere, **18** (0.352 g, 1.54 mmol) was dissolved in 1 mL of $CDCl_3$ and cooled to −30 °C in a dry ice/2-propanol bath.

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A solution of 81% MCPBA (0.327 g, 1.54 mmol) was dissolved in 5 mL of $CDCl_3$ and added slowly with stirring. After being stirred for 1 h at −30 °C, the product mixture was filtered at −45 °C under nitrogen, the filtrate transferred to an NMR tube, and NMR spectra were obtained.

Reaction of *S*-Phenyl 2,2-Dimethylpropanethiosulfinate (18) with 2,2-Dimethylpropanesulfinic Acid (20). A solution of 18 (0.042 g, 1.77 mmol) in 0.3 mL of $CDCl_3$ was mixed with an equimolar solution of **20** in 0.3 mL of $CDCl_3$ in a 5-mm NMR tube. The reaction was followed by ^1H NMR, starting 7 min after mixing, at 250 MHz. The presence of **5** and **19** was confirmed by comparison of ^1H NMR chemical shifts and TLC analysis done after 24 h.

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Registry No. **5**, 78607-80-4; **9**, 75142-07-3; **18**, 80318-99-6; **19**, 80319-01-3; **20**, 78607-81-5; **21**, 44820-66-8; **22**, 80319-02-4; **27**, 80319-00-2; **28**, 82323-60-2; **33**, 82323-61-3; **39**, 37552-63-9; **40**, 1679-08-9; **41**, 4972-29-6; *m*-chloroperoxybenzoic acid, 937-14-4; thiophenol, 108-98-5; neopentylsulfinyl chloride, 82215-38-1.

Cyclic Voltammetric Oxidation of Tetra-*tert*-butyltetrahedrane

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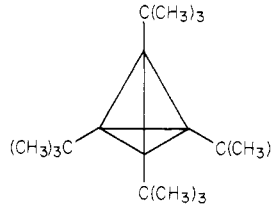
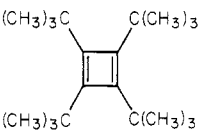
Cyclic voltammetric oxidation of tetra-*tert*-butyltetrahedrane (1; E_{pa} = 0.50 ± 0.10 V vs. SCE) is irreversible, producing the radical cation of tetra-*tert*-butylcyclobutadiene. No evidence for transient formation of other stable cation radical intermediates could be obtained in the electrooxidation of 1 and its subsequent formation of $2^{\cdot+}$. The oxidation is a one-electron process, and no waves attributable to redox reactions of the dication or dianion of cyclobutadiene could be observed.

Introduction

The remarkable stability of tetra-*tert*-butyltetrahedrane (**1**),[1] an air-stable solid melting at 135 °C, can be explained



1

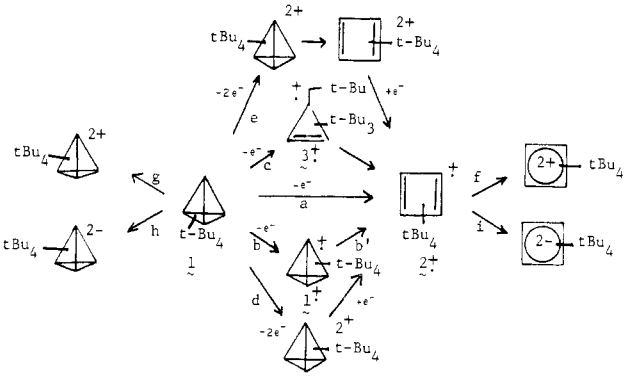


2

by the significant steric interaction introduced between the bulky *tert*-butyl groups when the tetrahedral symmetry of **1** is distorted. Accordingly, calculations[2] predict a significant barrier for the conversion of **1** to its valence isomer tetra-*tert*-butylcyclobutadiene (**2**). These same bulky substituents should also interfere with attacking reagents. Indeed, it is remarkably unreactive chemically, except with oxidizing reagents.[3]

Electron-transfer reactions, however, are much less sensitive to modest steric barriers, and the generation of ion radicals upon treatment with appropriate redox reagents should be possible. Upon chemical oxidation with $AlCl_3$, for example, a radical cation is generated from **1**

Scheme I. Possible Routes for the Rearrangement and Reactions of $1^{+\cdot}$



whose ESR spectrum is identical with that observed upon oxidation of **2**.[4] The efficiency of the conversion of $1^{+\cdot}$ to $2^{+\cdot}$ remains ambiguous, however.

In particular, whether the radical cation of $1^{+\cdot}$ has a discrete existence, whether Lewis-acid catalysis is required for the formation of $2^{+\cdot}$ from **1**, how rapidly $2^{+\cdot}$ is formed, and whether intermediates such as $3^{+\cdot}$, a tetra-*tert*-butylcyclopropenylcarbinyl cation radical, are involved are unknown. Furthermore, ESR, being insensitive to diamagnetic species, may not have detected formation of Hückel dicationic or dianionic redox products which might reasonably be postulated upon oxidation or reduction of this novel hydrocarbon.

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